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Silicon diffusion in germanium described by connecting point defect parameters with bulk properties

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Abstract

Silicon diffusion properties in germanium over a range of temperatures and pressures is technologically important for the formation of efficient nanoelectronic devices. Using experimental diffusivity data it is shown that elastic and expansivity data can describe the silicon diffusion coefficients in germanium in the temperature range of 827 K to 1176 K. In that respect the applicability of the $cB\Omega$ model, which assumes that the defect Gibbs energy is proportional to the isothermal bulk modulus and the mean volume per atom, is discussed.

Keywords: Germanium; diffusion; silicon

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1. Introduction

The interconnection of the defect Gibbs energy g^i and bulk materials properties in solids has led to different models.¹⁻¹⁰ The model by Varotsos and Alexopoulos³⁻⁹ (referred to as the cB Ω model) proposed that g^i is proportional to the isothermal bulk modulus B and the mean volume per atom Ω . Previous studies have established the efficacy of the cB Ω model to describe defect processes under hydrostatic pressure in numerous systems including alkali and silver halides, PbF₂, AgI, diamond, olivine, ZnO, LiH, silicon (Si), and others.¹¹⁻²⁰

Si technology dominated for numerous years due to the advantageous Si native oxide (i.e. SiO₂), which has superior materials properties as compared to GeO₂ in Ge technology.²¹⁻²⁵ The introduction of high dielectric constant (high- k) dielectrics has allowed the reconsideration of Ge for microelectronic applications.²⁶⁻²⁸ The defect processes of Ge are relatively undetermined compared to Si, however, recent studies have clarified most of the self- and dopant diffusion energetics and mechanisms.²⁹⁻³⁴ Interestingly, the diffusion of Si in Ge has received less attention than most diffusion processes.³⁵ In previous work R  is  nen *et al.*³⁶ determined that in the temperature range 650 to 900   C, Si diffusion in Ge can be described with an activation enthalpy of 2.9 eV and an exponential pre-factor of 0.24 cm² s⁻¹. S  dervall and Friesel³⁷ employed secondary ion mass spectrometry (SIMS) from a Si surface layer sputter deposited on a Ge wafer to determine an activation enthalpy of 3.47    0.07 eV and a pre-factor of 140    50 cm² s⁻¹ in the temperature range 650 to 930   C. Strohm *et al.*³⁸ implanted the radiotracer ³¹Si into Ge and then employed *in-situ* annealing and ion beam sectioning to determine the depth profiles and calculated an activation energy of 3.19 eV with a pre-factor of 43 cm² s⁻¹. Notably, previous studies did not consider in detail the possible existence of diffusion traps (carbon and oxygen)

in the host material. A more careful study was performed by Silvestri *et al.*³⁵, where the diffusion coefficient of Si in Ge over the temperature range of 550 to 900 °C can be described by a single activation energy (3.32 ± 0.03 eV) and a pre-factor of $42 \text{ cm}^2 \text{ s}^{-1}$. In the present study we model the Si diffusion coefficients in Ge using the cBΩ model.

2. Methodology

A. Point defect parameters

The point defect formation parameters can be defined by comparing a real (that is defective) crystal to an isobaric ideal (not defective) crystal.^{11,14} The isobaric parameters are defined in terms of the corresponding Gibbs energy (g^f) as:^{11,14}

$$s^f = - \left. \frac{dg^f}{dT} \right|_P \quad (1)$$

$$h^f = g^f - T \left. \frac{dg^f}{dT} \right|_P = g^f - Ts^f \quad (2)$$

$$v^f = - \left. \frac{dg^f}{dP} \right|_T \quad (3)$$

Where P is the pressure, T is the temperature; s^f , h^f and v^f represent the defect formation entropy, enthalpy and volume respectively.

For a monoatomic crystal with a single diffusion mechanism the self-diffusion process can be described by the activation Gibbs energy (g^{act}), which is the sum of the Gibbs formation (g^f) and the Gibbs migration (g^m) processes. The activation entropy s^{act} and the activation enthalpy h^{act} are defined by:^{11,14}

$$s^{\text{act}} = - \left. \frac{dg^{\text{act}}}{dT} \right|_P \quad (4)$$

$$h^{\text{act}} = g^{\text{act}} + Ts^{\text{act}} \quad (5)$$

The diffusion coefficient D can be defined by:

$$D = f a_0^2 \nu e^{-\frac{g^{act}}{k_B T}} \quad (6)$$

Where f is the diffusion correlation factor that depends upon the diffusion mechanism and the structure, a_0 is the lattice constant, ν is the attempt frequency and k_B is Boltzmann's constant.

B. The cBΩ model

The cBΩ model was initially developed and employed to describe vacancy Gibbs free formation energies. It was successfully applied to model diffusion in metals, where vacancies mainly facilitate atomic diffusion. In this model, the defect Gibbs energy g^i is related to the bulk properties of the solid via:³⁻⁹

$$g^i = c^i B \Omega \quad (7)$$

Where c^i is dimensionless.

$$s^i = c^i \Omega \left(\beta B + \left. \frac{dB}{dT} \right|_P \right) \quad (8)$$

$$h^i = c^i \Omega \left(B - T \beta B - T \left. \frac{dB}{dT} \right|_P \right) \quad (9)$$

$$v^i = -c^i \Omega \left(\left. \frac{dB}{dP} \right|_T - 1 \right) \quad (10)$$

Where β is the thermal (volume) expansion coefficient.

In the cBΩ model the diffusion coefficient can be derived at a temperature and pressure from a single experimental measurement. Combining Eqs. (6) and (7):

$$D = f a_0^2 \nu e^{-\frac{c^{act} B \Omega}{k_B T}} \quad (11)$$

From this relation using an experimentally determined diffusivity D_I value at T_1 the value of c^{act} can be calculated provided that the pre-exponential factor $f a_0^2 \nu$ can be calculated. In practice the calculation of the pre-exponential factor typically involves assuming the diffusion correlation factor (which depends upon the diffusion

mechanism and the structure) and the attempt frequency. The latter is usually approximated by the Debye frequency but leads to the introduction of errors.¹⁴ Applying this c^{act} the diffusivity D_2 at another temperature T_2 can be calculated using Eq. 11, assuming that the elastic data and expansivity are known for this temperature. As c^{act} is a constant that is assumed to be independent of temperature and pressure to a first approximation,^{11,14} its application in Eqs. (8)-(10) leads to the calculation of s^{act} , h^{act} and v^{act} at any T . Additionally, for constant T the D can be studied at any hydrostatic pressure.

The method of the single experimental measurement^{7,11,14} which was described above is not unique and other ways have been proposed to calculate c^{act} including the compensation law^{39,40} and the “mean value” method.^{16,19,41,42} The mean value method is employed to limit the dependence of c^{act} upon experimental uncertainties in the determination of the diffusivities, the expansivity and isothermal bulk modulus. In the mean value method a linear behavior of $\ln D^{Si}$ with respect to $\frac{B\Omega}{k_B T}$ implies that the cB Ω model is valid and the slope is c^{act} (refer to Eq. 11).

3. Results and discussion

A. Background

The cB Ω model is appropriate for describing atomic diffusion via a vacancy mechanism. Since the vacancy is the dominant intrinsic point defects in Ge that facilitates self and most dopant diffusion processes under intrinsic conditions,⁴³⁻⁴⁸ this model can also describe self- and Si diffusion in Ge.

Hüger *et al.*⁴⁴ determined that Ge self-diffusion in the temperature range 702 K to 1177 K can be described via:

$$D^V = 2.54e^{-\frac{3.13 \text{ eV}}{k_B T}} \cdot 10^{-3} m^2 s^{-1} \quad (12)$$

There is consensus between the experimental studies that Si diffusion in Ge is slower than Ge self-diffusion over the full temperature range and consequently the activation enthalpy is higher than that of self-diffusion. This in turn implies a reduced interaction potential between the Si atom and the vacancy that mediates the diffusion process. Previous density functional theory studies conclude that Si repels the vacancy in Ge.⁴⁷

The results of Silvestri *et al.*³⁵ in which Si diffusion in Ge for the temperature range 823 K to 1173 K can be described via the following Arrhenius relation:

$$D_{exp}^{Si} = 4.2e^{-\frac{3.32 \text{ eV}}{k_B T}} \cdot 10^{-3} m^2 s^{-1} \quad (13)$$

We choose to use the study of Silvestri *et al.*³⁵ data since they paid special attention to possible sources of non-equilibrium diffusion. In addition, the other data sets mentioned in the introduction are in close agreement with data of Ref. 35.

In the present study we adopt the results of Silvestri *et al.*³⁵ in which Si diffusion in Ge for the temperature range 823 K to 1173 K increase by about six orders of magnitude (refer to Table 1). Here we consider the same temperature range for which the expansivity data was taken from Kagaya *et al.*⁴⁹, whereas the isothermal bulk modulus data from Krishnan *et al.*⁵⁰

Figure 1 reports the Si diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$ verifying that the relation is linear (refer to Section 2B) and can be described by the following relation:

$$D_{cB\Omega}^{Si} = 2.2e^{-\frac{0.2909 B\Omega}{k_B T}} \cdot 10^{-2} m^2 s^{-1} \quad (14)$$

This c^{act} (0.2909 with a standard deviation of 0.02) in conjunction with the corresponding elastic and expansivity data is used in Eq. 11 to calculate the other diffusivity values with respect to temperature. Figure 2 is the Arrhenius plot for Si

diffusion in Ge obtained by experiment³⁵ and calculated by the cBΩ model as described above. It can be seen from this figure and Table 1 that the cBΩ model is in excellent agreement with experiment,³⁵ with experimental and calculated Si diffusion coefficients in Ge being within 3 %. Importantly, as we have established the validity of the cBΩ model for this system other defect properties (refer to Eqs. 8-10) can be calculated for different temperatures and hydrostatic pressures.

4. Conclusions

The understanding and control diffusion during device fabrication is important and the Si in Ge system is technologically relevant given the increasing interest to use $\text{Si}_{1-x}\text{Ge}_x$ epitaxial layers in Si-based integrated circuit technology. In the present study the applicability of the cBΩ model to describe Si diffusion in Ge is discussed. There is excellent agreement between the calculated and experimental Si diffusion coefficients in Ge for the wide temperature range considered. Si diffusion in Ge is dominated by vacancies and in future work the cBΩ model will be implemented in $\text{Si}_{1-x}\text{Ge}_x$ compositions where self-interstitials can become important and influence the diffusion processes. The extension of the model for non-uniform pressure fields can be technologically interesting for $\text{Si}_{1-x}\text{Ge}_x$ alloys and their application in nanoelectronic devices. This is because $\text{Si}_{1-x}\text{Ge}_x$ is placed at the channel of MOSFET devices under biaxial strain taking advantage of the higher carrier mobilities than in the unstrained material.

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Table 1. Characteristic calculated and experimental³⁵ Si diffusion coefficients in Ge alongside the elastic and expansivity data^{49,50} used in the cB Ω model.

T (K)	B (10 ¹¹ Nm ⁻²)	Ω (10 ⁻²⁹ m ³)	D_{exp}^{Si} (m ² s ⁻¹)	$D_{cB\Omega}^{Si}$ (m ² s ⁻¹)	$\frac{D_{cB\Omega}^{Si} - D_{exp}^{Si}}{D_{exp}^{Si}}$ (%)
827	0.709	2.289	$2.46 \cdot 10^{-20}$	$2.53 \cdot 10^{-20}$	3
877	0.703	2.292	$3.51 \cdot 10^{-19}$	$3.40 \cdot 10^{-19}$	-3
925	0.697	2.294	$3.42 \cdot 10^{-18}$	$3.35 \cdot 10^{-18}$	-2
975	0.690	2.298	$2.89 \cdot 10^{-17}$	$2.88 \cdot 10^{-17}$	0
1026	0.684	2.300	$2.06 \cdot 10^{-16}$	$2.05 \cdot 10^{-16}$	0
1074	0.678	2.303	$1.11 \cdot 10^{-15}$	$1.09 \cdot 10^{-15}$	-2
1126	0.671	2.306	$5.79 \cdot 10^{-15}$	$5.86 \cdot 10^{-15}$	1
1176	0.665	2.309	$2.48 \cdot 10^{-14}$	$2.48 \cdot 10^{-14}$	0

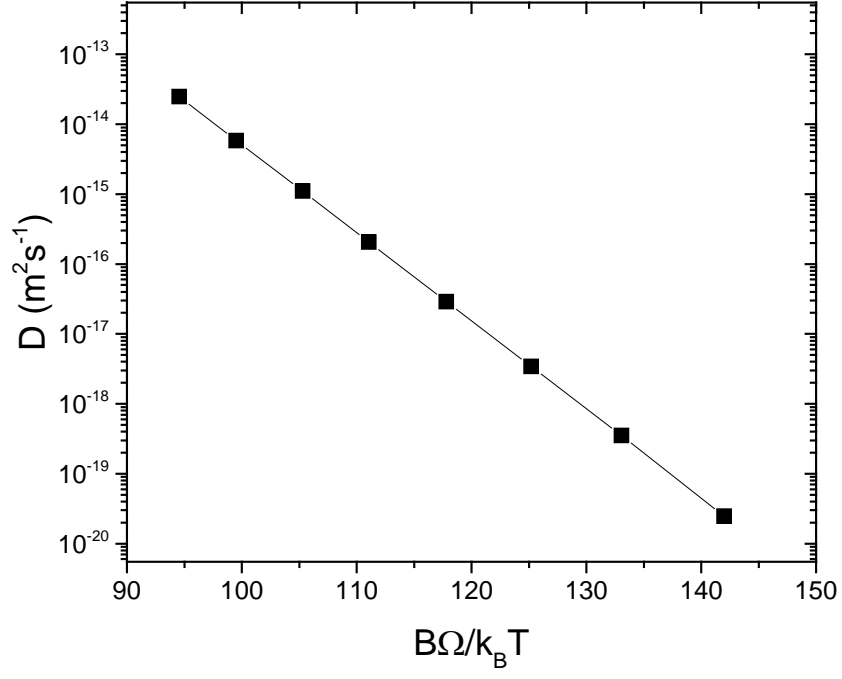


FIG. 1. The Si diffusion coefficients in Ge with respect to $\frac{B\Omega}{k_B T}$.

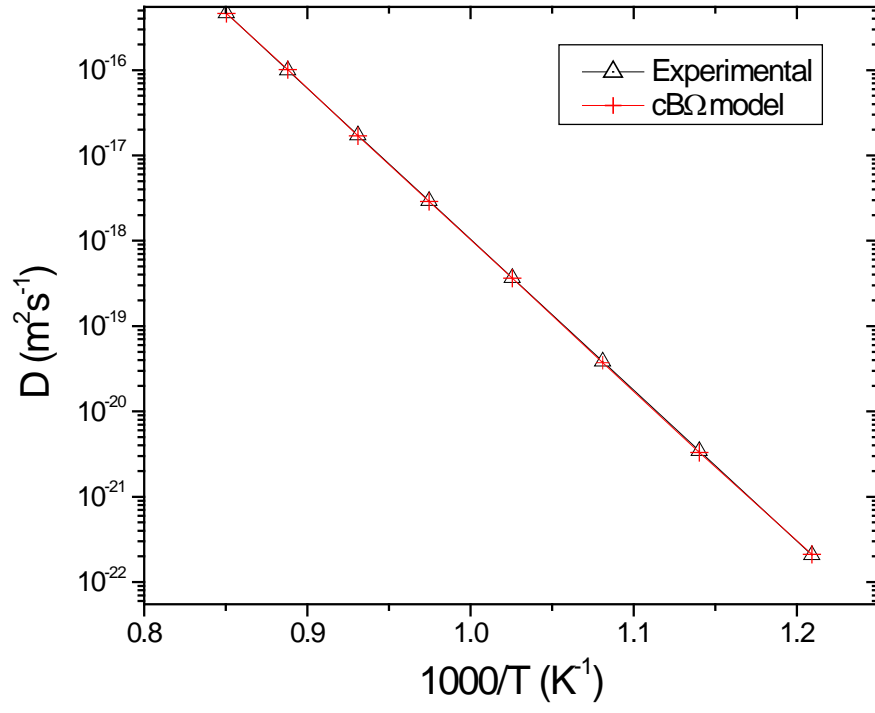


FIG. 2 The Arrhenius plot for Si diffusion in Ge obtained by experiment³⁵ and calculated by the cBΩ model.